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SOME ASPECTS OF CATALYTIC SYNTHESES IN RHODIUM CHEMISTRY

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ABBREVIATIONS

bipy	2,2'-bipyridyl	phen	1,10-phenanthroline
dmg	dimethylglyoximate	py	pyridine
en	ethylenediamine	tetmen	*N N N N'*-tetramethylethylenediamine
mal	malonate	trien	triethylenetetramine
ox	oxalate		

A INTRODUCTION

Substitutions at cobalt(III), rhodium(III) and iridium(III) centres in polar media, like water, are in general much slower than those for other oxidation states of the particular metal. Work in polar media naturally involves complexes of the more polar ligands, such as ammonia or amino acids. It has been known for some time that considerable rate enhancements, often useful synthetically, may be achieved through the addition of a redox reagent, and the oxidation states (for complexes containing essentially σ-bonding ligands like Cl^- or NH_3) most commonly invoked to rationalise this finding are shown in Table 1.

The critical factor in catalysis by one electron reducing agents at cobalt(III) is the formation of a cobalt(II) species, followed by a (usually) rate-determining electron transfer from this or a derivative to a cobalt(III) congener. Similar features underlie the catalysis of reactions of chromium(III) by the relatively inaccessible chromium(II).

The entirely different relations between oxidation states for rhodium (or iridium) as opposed to cobalt result in this one-electron reductive mechanism being non-catalytic* and it is the purpose of this present note to comment on the alternative way in which substitutions at rhodium(III) are catalysed.

B SYNTHETIC OBSERVATIONS

Delépine[1] found that alcohols containing the moiety RCHR'OH (where R or R', but not both, may be hydrogen) were very effective in promoting the formation of rho-

* Though a one-electron *oxidative* mechanism for iridium(III) may be useful.

TABLE 1

Oxidation states involved in redox catalysis of metal(III) reactions

	Co	Rh	Ir
More labile oxidised state		?	IV
↑ −e			
More inert state	III	III	III
↓ +e			
More labile reduced state	II	?	?
↓ +e			
More labile reduced state		I	I

dium(III) complexes from halorhodium(III) species and ligands Examples of complexes readily prepared from rhodium trichloride and the ligand using ethanol as catalyst are

(a) *trans*-$[RhL_4Cl_2]^+$, where L = pyridine[2], 3-, 4- or 5-substituted pyridine, isoquinoline, pyrimidine, pyrazole, thiazole or 5-substituted *N*-methylimidazole[3],

(b) $[RhL_5Cl]^{2+}$, where L = NH_3 or *N*-methylimidazole[3],

(c) $[Rh(mal)_3]^{3-}$ (ref 4), or

(d) *cis*-$[Rh(bipy)_2Cl_2]^+$★ (ref 5)

Two-electron reductants other than alcohols have been effective in synthetic work on rhodium(III) At various times hypophosphite ion[7], hydrazinium hydrochloride[7], borohydride ion[7], dihydrogen[8], carbon monoxide[9], ethylene[10] and a number of other reagents have been employed

One problem in elucidating such catalytic phenomena has been the common use of so-called "soluble rhodium trichloride" as the factor This has properties which vary with its provenance[11] and it is therefore reassuring that catalysis has been found in substitutions at rhodium(III) centres of a much better defined nature Some of these examples are listed in Table 2

Clearly such catalyses are a function of the formation of reduced species, and it is not therefore too surprising to find that dioxygen (which can serve as either a 1- or 2-electron oxidant) inhibits these reactions For example

(i) The reaction

$$trans\text{-}[Rh(py)_4Cl_2]^+ + 2\ Br^- \xrightarrow{H_2O} trans\text{-}[Rh(py)_4Br_2]^+ + 2\ Cl^- \qquad (1)$$

is very much slower in the presence of oxygen, showing complex kinetics, with an inhibition period[15] Some years ago we studied, in aqueous media, the exchange of labelled chloride in

$$[trans\text{-}[Rh(py)_4Cl_2]^+ + 2\ {}^{36}Cl^- \rightarrow trans\text{-}[Rh(py)_4\ {}^{36}Cl_2]^+ + 2\ Cl^- \qquad (2)$$

and obtained irreproducible results[17]; we now attribute this to the presence of oxygen

★ Prolonged refluxing of an aqueous ethanolic solution of rhodium trichloride and bipy gives only *cis*-$[Rh(bipy)_2Cl_2]^+$, whereas by allowing a completely deoxygenated aqueous ethanolic solution of rhodium trichloride and bipy to stand at room temperature for 1 week $[Rh(bipy)_3]^{3+}$ is formed[5] This is to be contrasted with the previously described preparation of $[Rh(bipy)_3]^{3+}$ which involved[6] heating rhodium trichloride in molten bipy (ca 180°)

TABLE 2
Substitutions at rhodium(III) catalysed by 2-electron reductants

Catalyst	Factor	X [d]	Product	Ref	Notes
Trace BH_4^-	*trans*-$[Rh(en)_2Cl_2]^+$	Br^-	*trans*-$[Rh(en)_2Br_2]^+$	12	b
Trace BH_4^-	1,2,3,6-$[RhtrienCl_2]^+$	Br^-	1,2,3,6-$[RhtrienBr_2]^+$	14	b
Trace BH_4^-	1,2,3,4-$[RhtrienCl_2]^+$	Br^-	1,2,3,4-$[RhtrienBr_2]^+$	14	b
Trace BH_4^-	1,2,4-$[Rh(py)_3ClOX]$	Br^- or I^-	1,2,4-$[Rh(py)_3XOX]$	12	
H_3PO_2	*trans*-$[Rh(dmg)_2Cl_2]^-$	py	*trans*-$[Rh(dmg)_2pyCl]$	7	
Ethanol	*trans*-$[Rh(py)_4Cl_2]^+$	Br^-	*trans*-$[Rh(py)_4Br_2]^+$	15	c
Ethanol	*trans*-$[RhL_4Cl_2]^+$	Br^-	*trans*-$[RhL_4Br_2]^+$	3	d
Ethanol	$[Rh(H_2O)Cl_5]^{2-}$	py	*trans*-$[Rh(py)_4Cl_2]^+$	16	c
N_2H_4 HCl	$[RhphenCl_4]^-$	phen	*cis*-$[Rh(phen)_2Cl_2]^+$	5	
N_2H_4 HCl	*cis*-$[Rh(AA)_2Cl_2]^+$	AA	$[Rh(AA)_3]^{3+}$	5	f
	(+)-*cis*-$[Rh(phen)_2Cl_2]^+$	OH^-	(±)-*cis*-$[Rh(phen)_2Cl(OH)]^+$	5	g

[a] X is the entering group (usually halide ion)
[b] This reaction is *not* catalysed by ethanol, it is also interesting that substitution at $[Rh(NH_3)_5Cl]^{2+}$ is not catalysed by borohydride[13]
[c] Whereas primary or secondary alcohols >CHOH possessing the "hydridic" grouping (in the context of 2-electron reduction of transition metal ions) are effective catalysts, *t*-butanol, with no such grouping, is *not*[15]
[d] L = thiazole, this reaction is some 500 times faster in 30% ethanol than in water[12] Qualitatively there is also marked catalysis by ethanol of this substitution when L = alkylpyridine, acetylpyridine, pyrimidine, pyrazole or isoquinoline[3]
[e] Presumably via catalysis of some or all of the individual steps in the process, $[Rh(H_2O)Cl_5]^{2-}$ $[Rh(py)_2Cl_4]^- \rightarrow$ 1,2,6-$[Rh(py)_3Cl_3] \rightarrow$ *trans*-$[Rh(py)_4Cl_2]^+$ We know that at least the final reaction is catalysed[8] However, such reactions are not always catalysed since it is possible to recover 1,2,6-$[Rhpy_3(N_3)_3]$ unchanged from a boiling aqueous ethanolic pyridine solution[12]
[f] AA = bipy or phen This constitutes a simple preparation of $[Rh(AA)_3]^{3+}$ which has previously only been obtained under much more forcing conditions[6]
[g] This reaction is inhibited by dioxygen Thus a solution of (+)-*cis*-$[Rh(phen)_2Cl_2]^+$ at 90° (pH 13) for 5 min retains 90% activity, whereas reaction of the same solution, which has been first *rigorously degassed*, occurs with complete racemisation under the same conditions[5]

Similarly, the substitution by bromide is much slower in the presence of chlorite ion

(ii) A number of apparent catalyses of reaction (1) by such reductant gases as carbon monoxide, ethylene and dihydrogen must be attributed, at least in part, to the removal of dioxygen by the gas stream, since we have found similar effects with cyclopropane, dinitrogen and argon

(iii) The currently uncertain state of dioxygen effects on the catalytic reactivity of Wilkinson's compound, $[Rh(PPh_3)_3Cl]$, is also related to this marked interference by dioxygen[18,19]

As would be expected from the conflicting effects of ethanol and dioxygen described above, the situation in aerobic ethanolic systems is complicated[15]

TABLE 3
Variation in properties of the electrochemically reduced species, I, with pH

	pH 2	pH 7	pH 13
$E_{½}$ [a]	∞	ca 2 min (25°)	Instant (25°)
$W_{½}$ [b]	4 Hz	5 Hz	∞
k [c]	4 18 × 10^{-5} sec^{-1}	Complete in 5 min	Very rapid

[a] Half-life for oxygen uptake
[b] Width at half height for NMR signal due to Rh–H (τ30 6)
[c] Rate constant at 25° for the reaction
trans-$[Rh(en)_2Br_2]^+ + 2\ Cl^-$
with I added, *trans*-$[Rh(en)_2Cl_2]^+$ I = 5 1

C NATURE OF THE REDUCED SPECIES AND MECHANISM OF CATALYSIS

Several observations provide a link between this efficiency of 2-electron reductants as catalysts and the likely catalytic species On treatment of several halo-rhodium(III) complexes with borohydride, hydridorhodium(III) complexes are formed [20–22] These show the usual infrared absorption due to ν(Rh–H) at ca.2100 cm^{-1} and in solution show the characteristic high field signal (ca.τ30) which is split into a doublet by ^{103}Rh (100% abundance, $I = ½$) ^2J(Rh–H) ca.30 Hz

From electrochemical studies, it has recently emerged that (at least in water) the actual 2-electron reduced state is an equilibrium between hydrido-rhodium(III) complexes and the product of reductive elimination[26] Thus, electrochemically

$$trans\text{-}[Rh(en)_2Cl_2]^+ + 2\,e \xrightarrow[pH\ 7]{-1.0\ V} \underset{I}{trans\text{-}[Rh(en)_2H(OH)]^+} + 2\ Cl^- \qquad (3)$$

I can be obtained as a solid by addition of sodium tetraphenylborate, whereas with the more basic ligand tetmen, *trans*-$[Rh(tetmen)_2H(OH_2)]^{2+}$ is obtained under the same conditions[27]

The 1-electron reduced species has also been detected in these studies[23] It seems that the essential mechanism of its formation is

$$[Rh^{III}] \xrightarrow{1\,e} [Rh^{II}] \xrightarrow{fast} ½[Rh^{II}]_2$$

The dirhodium(II,II) species is diamagnetic and presumably has a rhodium–rhodium bond, although it was not possible to detect ν(Rh–Rh) by Raman spectroscopy due to rapid decomposition upon irradiation by the exciting source (He/Ne laser) The ligands *trans* to the rhodium–rhodium bond are very labile, although no dissociation of ethylenediamine was detected However, in some cases ligands *cis* to the rhodium–rhodium bond can also be replaced, viz

$$\xrightarrow{H^+/H_2O} [(H_2O)_8Rh_2S_2] \text{ (ref 24)}$$

$$[(RCOO)_4RH_2S_2] \longrightarrow$$
(S = solvent)

$$\xrightarrow[Dmg/PPh_3]{} [(PPh_3)dmgRh(RCOO)_2^- \quad Rhdmg(PPh_3)] \text{ (ref 25)}$$

In water, slow dismutation occurs, viz

$$[(H_2O)(en)_2RhRh(en)_2(H_2O)]^{4+} \rightarrow [Rh(en)_2(H_2O)(OH)]^{2+} + [Rh(en)_2H(OH_2)]^{2+}$$

and it seems unlikely (but not impossible, in view of these rapid exchange reactions) that rhodium(II) is involved in the reductive catalyses of rhodium(III) reactions

In solution, the 2-electron reduced species from *trans*-$[Rh(en)_2Cl_2]^+$ shows properties which vary with pH (Table 3). There are two possible explanations, which are based on the equilibria

$$\underset{II}{trans\text{-}[Rh(en)_2H(OH_2)]^{2+}} \overset{K_1}{\rightleftharpoons} H^+ + \underset{I}{trans\text{-}[Rh(en)_2H(OH)]^+} \overset{K_2}{\rightleftharpoons} \underset{III}{[Rh(en)_2]^+} + H_2O \qquad (4)$$

(1) That $K_2 = 0$ and that the reactivities of I and II differ by many orders of magnitude toward (a) dioxygen [I reacts fast, II not at all[1]]; (b) exchange with water [II slow, giving a doublet signal for Rh–H; I so fast that the signal is broadened completely], and (c) catalysis of the prototype halide exchange

(2) That K_2 is finite and that $[Rh(en)_2]^+$ is the reactive species

The latter explanation seems very much more probable, and we have direct evidence for it in the case of the pyridine complexes, viz

$$trans\text{-}[Rh(py)_4Cl_2]^+ + BH_4^- \xrightarrow{LiOH} \underset{IV}{trans\text{-}[Rh(py)_4HCl]^+} + Cl^- \qquad (5)$$

$$trans\text{-}[Rh(py)_4HCl]^+ + \text{base} \rightarrow \underset{V}{[Rh(py)_4]^+} + \text{base HCl} \qquad (6)$$

$$[Rh(py)_4]^+ + XY \rightarrow \underset{VI}{trans\text{-}[Rh(py)_4XY]^+} \; (XY = Cl_2, I_2, HCl, HBr) \qquad (7)$$

$$\underset{V}{[Rh(py)_4]^+} + H\,OH \rightleftharpoons \underset{VII}{trans\text{-}[Rh(py)_4H(OH)]^+} \qquad (8)$$

All the complexes IV–VII have been isolated as solid salts and have been completely characterised Furthermore, we find that *trans*-$[Rh(py)_4H(OH)]^+$ undergoes rapid exchange with D_2O in neutral conditions, presumably via the reduced intermediate, $[Rh(py)_4]^+$.

$$trans\text{-}[Rh(py)_4H(OH)]^+ + D\,OD \rightleftharpoons trans\text{-}[Rh(py)_4D(OD)]^+ + H\,OH \qquad (9)$$

We also find that $[Rh(py)_4]^+$ catalyses substitutions in both *trans*-$[Rh(py)_4Cl_2]^+$ and *trans*-$[Rh(en)_2Cl_2]^+$, whereas the dominant form in acid solution, *trans*-$[Rh(py)_4H(OH_2)]^{2+}$, does not

Thus the control of the reactions of rhodium(III) complexes, in the presence of reducing agents stems from the redox equilibrium

$$Rh^{III} + (2e)\ RED \overset{K_{10}}{\rightleftharpoons} Rh^{I} + OX \tag{10}$$

$$Rh^{I} + HY \overset{K_{11}}{\rightleftharpoons} [HRh^{III}Y] \tag{11}$$

$$Rh^{I} + HYH^{+} \overset{K_{12}}{\rightleftharpoons} [HRh^{III}(YH)]^{+} \tag{12}$$

We may note that we expect the oxidising power to increase from anion (e g OH^-, NH_2^-) to neutral species (OH_2, NH_3) to cation (H_3O^+, NH_4^+), i e $K_{12} > K_{11}$ Thus rhodium(III) hydrides are the dominant species in highly protic solvents (acid) whereas rhodium(I) will become important in the absence of protons (neutral or alkaline conditions) It is this latter species which is the effective catalyst and the mechanism is similar to the 2-electron, (d^8–d^6) redox mechanism found in Pt^{IV} chemistry by Basolo et al [28] The control in the catalytic efficiency of various reductants is due to equilibrium 10, where, other things being equal, the stronger the reductant the more rhodium(I) will be present

Equilibria (11) and (12) can be extended to other systems such as the well known hydrido-pentamminerhodium(III) cation The reaction of $[Rh(NH_3)_5H]^{2+}$ with water has been regarded as an example of the strong *trans*-effect of the hydride ligand, viz

$$[Rh(NH_3)_5H]^{2+} + H_3O^+ \rightleftharpoons \textit{trans}\text{-}[Rh(NH_3)_4H(OH_2)]^{2+} + NH_4^+ \tag{13}$$

However, the above reaction may be thought of as arising from two redox equilibria, viz

$$[NH_3)Rh(NH_3)_4H]^{2+} \rightleftharpoons [Rh(NH_3)_4]^+ + NH_4^+ \tag{14}$$

and

$$[Rh(NH_3)_4]^+ + H_3O^+ \rightleftharpoons \textit{trans}\text{-}[(H_2O)Rh(NH_3)_4H]^{2+} \tag{15}$$

which might also better explain the reactivity of $Rh(NH_3)_5H]^{2+}$ and $[Rh(NH_3)_4H(OH_2)]^{2+}$ towards olefins [22] Similar reasoning also explains the reactivity of $[Rh(CN)_5H]^{3-}$ and *trans*-$[Rh(CN)_4H(OH_2)]^{2-}$

Further work will be necessary to evaluate such possibilities but the general situation in rhodium(III) chemistry is now fairly clear There are still some problems which do not fit easily into current schemes, these are

(i) The intimate mechanism of addition to rhodium(I) (and of course elimination from $Rh^{III}HX$) of HX The addition of hydrogen to $[Rh(py)_4]^+$, rather unusually, gives *trans*-$[Rh(py)_4H_2]^+$ In the polar solvents considered here, products such as $[Rh(py)_4HX]^+$ and $[Rh(en)_2HX]^+$ (X = OH^-, halide) are *trans* isomers, but, in view of the catalytic transformation by borohydride of *cis*-$[RhtrienCl_2]^+$ to *cis*-$[RhtrienBr_2]^+$ *without stereochemical change* this need not constitute a mechanistic proof

(ii) How, when reduced solutions are treated with dioxygen (or trioxygen) do we finish with dimeric superoxo complexes [26,29] ? The reaction of dioxygen with rhodium(I) is complementary

$$X^- + [Rh^{I}L_4]^{n+} + O_2 \rightleftharpoons [XRh^{III}L_4O_2]^{(n-1)+} \ (+ H^+)$$

$$\downarrow$$

$$[XRh^{III}L_4(OOH)]^{n+} \tag{16}$$

(iii) The intimate mechanism of electron transfer is still uncertain We know that chlorine can serve as a bridge for the net movement of 0 electrons (Pt^{II}–Cl–Pt^{II}), 1 electron (Co^{III}–Cl–Cr^{II}, Cr^{III}–Cl–Cr^{II}) and for 2 electrons (Pt^{IV}–Cl–Pt^{II}, Rh^{III}–Cl–Rh^{I}) What orbitals are involved?

(iv) How does hydride exert its *trans*-effect in these octahedral systems? The two extreme mechanisms may be represented by

(a) a pseudo S_N1 mechanism, viz

$$\begin{array}{l} H{-}M{-}X \rightarrow (H{-}M)^+ + X^- \\ \qquad\qquad \downarrow Y^- \\ \qquad\quad H{-}M{-}Y \end{array} \qquad (17)$$

(b) a redox mechanism viz

$$B \curvearrowright H{-}\overset{\curvearrowright}{M^n}{-}\overset{\curvearrowright}{X} \rightarrow BH^+ + M^{n-2} + X^- \qquad (18)$$

$$BH^+ + M^{n-2} + Y^- \rightarrow B: + HMY \qquad (19)$$

Currently, our evidence in rhodium(III) chemistry favours the latter situation

Our present knowledge of the reactions of the reduced rhodium complexes is summarised in Fig 1, to which the notes below refer

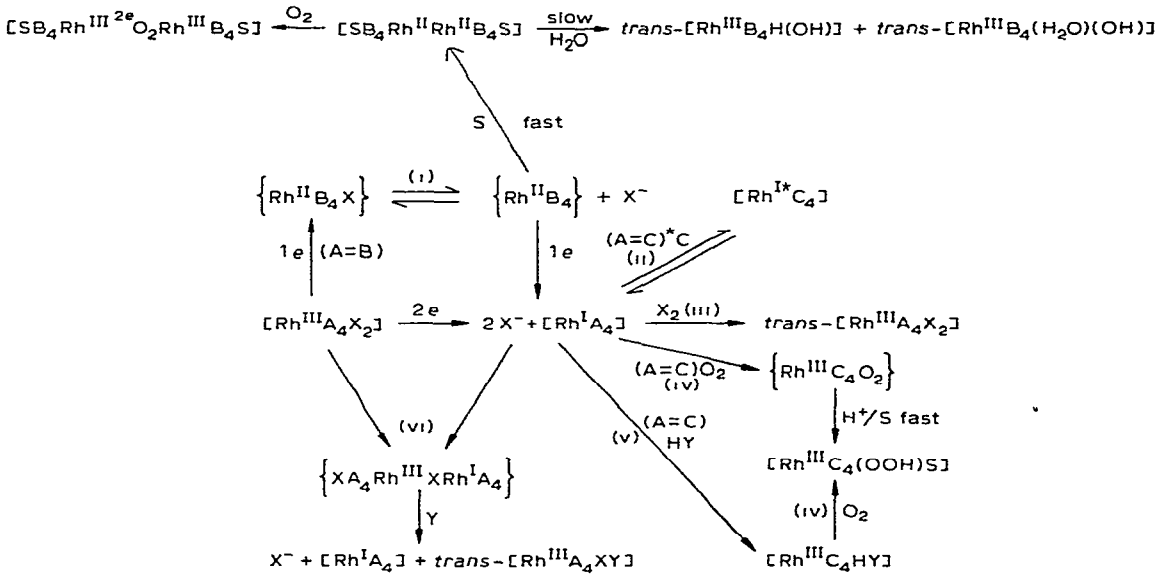

Fig 1 Summary of reactions of reduced rhodium complexes A = en or py, B = en, C = py, X = halide, S = solvent Compounds in parentheses { } are presumed intermediates

NOTES

(i) Subsequent dimerisation is not always fast, rhodium(II) monomeric species are known, e g. dichlorotris(tri-*o*-methoxyphenylphosphine)rhodium(II) (ref 30)

(ii) A number of exchanges at rhodium(I) centres are known to be extremely rapid and proceed via a 5-coordinate intermediate, viz eqns (20) (ref 31) and (21) (ref 32)

$$[Rh(PF_3)(PPh_3)_2Cl] \begin{array}{l} \xrightarrow{*PF_3} [Rh(*PF_3)(PPh_3)_2Cl] \\ \xrightarrow{*PPh_3} [Rh(PF_3)(*PPh_3)_2Cl] \end{array} \quad (20)$$

$$[Rh(py)_4]^+ \xrightarrow{D_5-py} [Rh(D_5-py)_4]^+ \quad (21)$$

Rund [16] found, in the pyridine system, an inhibition by phen, which he attributed to its "scavenging" the rhodium(I)

(iii) $X_2 = Cl_2, Br_2, I_2$

(iv) The actual species which reacts with dioxygen is not entirely clear, e g $[Rh(en)_2]^+$ reacts rapidly with dioxygen, but the hydrido-complexes, *trans*-$[Rh(en)_2HY]^+$ do not However, while $[Rh(py)_4]^+$ reacts rapidly with dioxygen in this case, the hydrido-complex, *trans*-$[Rh(py)_4HCl]^+$ also does so, *in the solid state*, giving quantitatively [32] *trans*-$[Rh(py)_4Cl(OOH)]^+$

(v) HY = H OH_2^+, HCl or HBr additions are carried out in ethanol

(vi) We have some qualitative indications as to which ligands X, can serve as bridging ligands for the 2-electron transfer Certainly halides can, whereas azide (at least in 1,2,6-$[Rh(py)_3(N_3)_3]$) and hydroxide (in *trans*-$Rh(py)_4Cl(OH)]^+$) cannot

The nature of the final products under a particular set of catalytic conditions may be rationalised in terms of two processes the lability of rhodium(I) and the subsequent formation of the X-bridged intermediate, $[Rh^{III}XRh^I]$ Calling the Rh–X–Rh direction z, it seems that the ligands in the x and y planes in $[Rh^{III}XRh^I]$ are much less labile than those on the z axis However, it is just these ligands (x y axis) which in the rhodium(I) species are labile Clearly, the relevant competing rates are those which control the fate of $[Rh^I]$, i e

$$[Rh^IA_4] \begin{array}{l} \xrightarrow{k\ \text{association}} [XA_4Rh^{III}XRh^IA_4] \\ \xrightarrow{k\ \text{exchange (+ A')}} [Rh^IA_4A'] \text{ etc} \end{array}$$

Where $k_{assoc} \gg k_{exch}$ we have catalysis of nucleophilic displacement of the group X, e g

$$trans\text{-}[Rh(py)_4Cl_2]^+ + OH^- \xrightarrow[\text{or } BH_4^-]{EtOH} trans\text{-}[Rh(py)_4Cl(OH)]^+ + Cl^- \quad (22)$$

$$trans\text{-}[Rh(py)_4Cl_2]^+ + X^- \xrightarrow[\text{or } BH_4^-]{EtOH} trans\text{-}[Rh(py)_4X_2]^+ \ [(X = Br^- \text{ or } I^-)] \quad (23)$$

In cases where $k_{assoc} \ll k_{exch}$ we have catalysis of substitution in the xy plane, e g with cold aqueous BH_4^-

$$trans\text{-}[Rh(py)_4Cl_2]^+ + CNO^- \xrightarrow{BH_4^-} cis\text{-}[Rh(py)_3Cl(NCO)_2] \quad (24)$$

$$trans\text{-}[Rh(py)_4Cl_2]^+ + ox \xrightarrow{BH_4^-} [Rh(py)_3Cl(ox)] \quad (25)$$

$$trans\text{-}[Rh(py)_4Cl_2]^+ + N_3^- \xrightarrow{BH_4^-} 1,2,6\text{-}[Rh(py)_3(N_3)_3 \quad (26)$$

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