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**RESEARCH ARTICLE**

# Oxidorhenium(V) and Imidorhenium(V) Complexes of Pyridylpyridazine:Oxygen Atom Transfer, Oxidation and Substitution Involving Oxido, Phosphine Oxide and Phosphine Coordination

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**Abstract:** Oxido and imido complexes of type $Re^VOCl_3(dppz)$ and $Re^V(NPh)Cl_3(dppz)$ having *meridional* geometry (where dppz is 3,6-di(2-pyridyl)pyridazine) have been isolated and characterized. The oxygen atom transfer from $Re^VOCl_3(dppz)$ to $PPh_3$ has afforded $Re^{III}(OPPh_3)Cl_3(dppz)$ which on chemical oxidation by $HNO_3$ yielded $[Re^{IV}(OPPh_3)Cl_3(dppz)]ReO_4$. Treatment of $Re^{III}(OPPh_3)Cl_3(dppz)$ with $PPh_3$ has furnished *facial* $Re^{III}(PPh_3)Cl_3(dppz)$. The second-order rate law and large negative entropy of activation (-15.8 eu) of the oxygen atom transfer reaction of $Re^VOCl_3(dppz)$ with $PPh_3$ is consistent with an associative pathway initiating through nucleophilic phosphine attack to $Re{\equiv}O$ $\pi^*$ orbitals.

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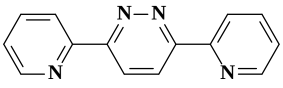
**Keywords**: Oxidorhenium(V), Imidorhenium(V), Pyridylpyridazine, Oxygen atom transfer

## Introduction

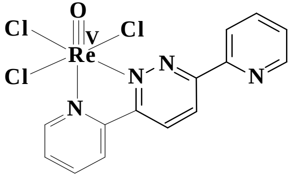
In recent years the chemistry of rhenium has moved toward new applications in the therapeutic nuclear medicine and new complexes have been developed for the selective delivery of cytotoxic radionuclides $^{186}Re$ and $^{188}Re$ to tumors[1]. Formation of oxido moieties constitute a dominant feature in the higher oxidation states of rhenium[2]. The oxygen-atom transfer ability of the oxidorhenium(V) moiety $Re^VO$ has been known for a long time and the nature and scope of the process have attracted significant recent attention[3].Transfer reactions promoted by enzymatic oxido sites based on iron, molybdenum, and tungsten are important in the chemistry of life[4]. Rhenium is not a biometal in the same sense, but as an element in the periodic group next to that of molybdenum and tungsten, transfer reactions involving $Re^{V}O$ are of value as potential models[5].

The ligand 3,6-di(2-pyridyl)pyridazine (dppz, **1**) is well documented to form mononuclear and cyclometallated, asymmetrically bridged dinuclear ruthenium complexes[6] and also as combination of multiple metal complexes into a single heterometallic architecture[7]. The copper(I) complex containing the ligand dppz can represent models for dicopper-containing proteins[8]. The ligand is capable of forming [2x2] grid-like metal complexes with copper(I) and silver(I) ions[9].

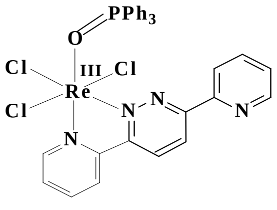
To the best of our knowledge nothing is known about the oxidorhenium chemistry of dppz. Herein, we report the successful synthesis and characterization of $Re^{V}O$ complex $ReOCl_3$(dppz), **2** incorporating chelation by 3,6-di(2-pyridyl)pyridazine, which reacts with triphenyl phosphine furnishing stable rhenium(III) phosphine oxide species $Re(OPPh_3)Cl_3$(dppz), **3**. The rates and activation parameters of the oxygen atom transfer are reported. The oxidorhenium(V) complex reacts with aromatic primary amine furnishing imidorhenium(V) complex $Re(NPh)Cl_3$(dppz), **4**. The rhenium(III) phosphine oxide complex upon metal oxidation by dilute nitric acid affords the rhenium(IV) congener $[Re(OPPh_3)Cl_3(dppz)]ReO_4$, **5**. Coordinated rhenium(III) phosphine oxide are replaceable by tertiary phosphine furnishing $Re(PPh_3)Cl_3$(dppz), **6** but with geometrical transformation (*meridional→facial*). The spectral, electrochemical and magnetic characterization of the complexes reported in the article.



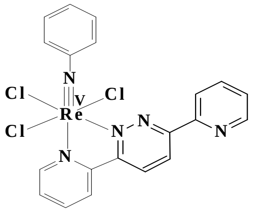
**dppz, 1**



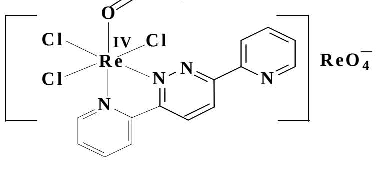
**$ReOCl_3$(dppz), 2**



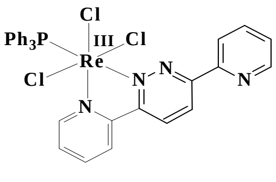
**$Re(OPPh_3)Cl_3$(dppz), 3**



**$Re(NPh)Cl_3$(dppz), 4**



**$[Re(OPPh_3)Cl_3(dppz)]ReO_4$, 5**



**$Re(PPh_3)Cl_3$(dppz), 6**

## Experimental

The concerned ligand 3,6-di(2-pyridyl)pyridazine (dppz, **1**) was synthesized using available method[10]. The equimolecular reaction of dppz with $ReOCl_3(PPh_3)_2$ in stirred benzene solution at room temperature afforded the orange-yellow oxido complex **2** (Eq. 1).

$$ReOCl_3(PPh_3)_2 + dppz \rightarrow ReOCl_3(dppz) + 2PPh_3 \quad (1)$$

Use of dichloromethane as the solvent (in which **2** is soluble) in the above synthesis leads to further reaction, (Eq. 2), furnishing violet coloured complex **3** which can also be synthesized from preisolated **2** and $PPh_3$. The oxido oxygen atom in **2** is readily substituted by the imido function upon reacting with aniline ($PhNH_2$) in boiling benzene to produce the blue coloured imido species **4**. The transformation which is essentially of acid-base type is stated in Eq 3.

$$ReOCl_3(dppz) + PPh_3 \rightarrow Re(OPPh_3)Cl_3(dppz) \quad (2)$$

$$ReOCl_3(dppz) + PhNH_2 \rightarrow Re(NPh)Cl_3(dppz) + H_2O \quad (3)$$

Electrochemical experiments (vide infra) revealed that the rhenium(IV) congener of **3** can be electrogenerated in solution. This prompted us to examine their chemical oxidation. Indeed **3** was readily oxidized by 0.1N $HNO_3$ in acetonitrile solution furnishing 1:1 electrolytic **5** (Eq. 4) as yellow solid. It is unclear how the $ReO_4^-$ anion originated from the starting material but this behaviour has precedence in rhenium chemistry[5,11]. Treatment of a solution of **3** with six fold excess of $PPh_3$ in boiling benzene yielded green coloured **6** (Eq. 5). The reaction is attended with geometrical transformation (*mer*→*fac*).

$$2Re(OPPh_3)Cl_3(dppz) + HNO_3 \rightarrow [Re(PPh_3)Cl_3(dppz)]ReO_4 \quad (4)$$

$$Re(OPPh_3)Cl_3(dppz) + PPh_3 \rightarrow Re(PPh_3)Cl_3(dppz) + OPPh_3 \quad (5)$$

### *Materials*

3,6-Di(2-pyridyl)pyridazine was synthesized by reported method[10]. The purification and drying of dichloromethane and acetonitrile for spectral and electrochemical work was done as before[12]. Benzene was distilled over sodium before use. All other chemicals and solvents were of reagent grade and were used as received.

### *Physical measurements*

UV-Vis spectral measurements were carried out with a Shimadzu UVPC 1601 spectrometer fitted with thermostated cell compartments. IR spectra (4000-100 $cm^{-1}$) were recorded in KBr disk with the help of Perkin Elmer L-0100 and Nicolet Magna IR 750 Series II spectrometers. Proton NMR spectra were recorded on a Bruker FT 300 MHz spectrometer. In $^1H$ NMR the spin-spin structures are abbreviated as follows: s, singlet; d, doublet; t, triplet: m, multiplet and b, broad. Electrochemical measurements were performed under nitrogen atmosphere on a CH 620A electrochemical analyzer, using a platinum working electrode. The supporting electrolyte was tetraethylammonium perchlorate (TEAP), and the potentials are referred to the saturated calomel electrode (SCE) without junction correction. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 series II elemental analyzer. Solution electrical conductivity was measured in methanol (~$10^{-3}$ M solution) with a Phillips PR 9500 bridge using a platinized electrode (cell constant of 1.05). Room-temperature magnetic susceptibilities of powders were measured with a model 155 PAR vibrating sample magnetometer.

## Synthesis

### *Synthesis of $ReOCl_3(dppz)$, (**2**)*

To a suspension of $ReOCl_3(PPh_3)_2$ (100 mg, 0.12 mmol) in 50 mL benzene 28 mg (0.12 mmol) of dppz was added and the resulting mass was stirred at room temperature for 4 h. The orange-yellow solid $ReOCl_3(dppz)$ appeared was collected by filtration, washed thoroughly with benzene and finally dried in vacuum over fused $CaCl_2$. Yield: 46 mg(70%). Anal. Calcd. for $C_{14}H_{10}Cl_3N_4ORe$: C, 30.91; H, 1.86; N, 10.31. Found: C, 30.88; H, 1.90; N, 10.34. UV-vis ($\lambda_{max}$, nm ($\varepsilon$, $M^{-1}$ $cm^{-1}$), $CH_2Cl_2$ solution): 760(310), 470(3100), 310(12200).

$^1$H NMR δ in (DMSO-$d_6$): 8.84(d, 1H, J=6.2Hz), 8.71(d, 1H, J=7.2Hz), 8.58(d, 1H, J=7.6Hz), 8.43(d, 1H, J=7.1Hz), 8.30(t, 1H, J=7.4Hz), 7.96(d, 1H, J=7.5Hz), 7.76(t, 2H, J=8.6Hz), 7.51(t, 1H, J=6.8Hz), 7.36(d, 1H, J=7.1Hz).

### *Synthesis of Re(OPPh$_3$)Cl$_3$(dppz),* **(3)**

To 65 mg (0.12 mmol) of complex **2** in dichloromethane solution 63 mg of (0.24 mmol) PPh$_3$ was added and the solution was stirred magnetically at room temperature for 3 h. During the reaction the solution colour changed from orange yellow to violet. The solution was subjected to chromatography on a silica gel column (25x1 cm, 60-120 mesh). Excess PPh$_3$ was eluted with benzene. The violet band that followed was eluted with a benzene-acetonitrile (50:3) mixture. Solvent removal from the eluate under reduced pressure afforded Re(OPPh$_3$)Cl$_3$(dppz) as violet solid. Yield: 73 mg(75%). Anal. Calcd. for $C_{32}H_{25}Cl_3N_4OPRe$: C, 47.62; H, 3.13; N, 6.95. Found: C, 47.70; H, 3.15; N, 6.94. UV-vis ($\lambda_{max}$, nm (ε, M$^{-1}$ cm$^{-1}$), $CH_2Cl_2$ solution):730(5100), 580(3200), 470(5600). $^1$H NMR δ in (CDCl$_3$): dppz, 28.03(b, 1H), 23.15(b, 1H), 10.20(d, 1H, J=6.9Hz), 9.78(d, 1H, J=7.2Hz), 9.28(t, 1H, J=7.0Hz), 9.08(d, 1H, J=5.8Hz), 7.29(t, 1H, J=7.4Hz), 6.89(d, 1H, J=7.1Hz), -1.31(b, 1H), -1.86(b, 1H); PPh$_3$ 7.53(t, 6H, J=7.3Hz), 7.09(t, 3H, J=7.6Hz), 6.69(m, 6H).

### *Synthesis of Re(NPh)Cl$_3$(dppz),* **(4)**

To 65 mg (0.12 mmol) of complex **2** in dichloromethane 56 mg (0.60 mmol) aniline in 50 mL benzene was added and the mixture was heated to reflux for 1.5 h, affording a blue solution. The solvent was then removed under reduced pressure, and the mass thus obtained was subjected to chromatography on a silica gel column (20x1 cm, 60-120 mesh). Excess aniline was eluted with benzene. A blue band was then eluted with a benzene-acetonitrile (25:1) mixture. Solvent removal from the eluate under reduced pressure afforded Re(NPh)Cl$_3$(dppz) as a blue solid. Yield: 60 mg(81%). Anal. Calcd. for $C_{20}H_{15}Cl_3N_5Re$: C, 38.88; H, 2.45; N, 11.35. Found: C, 38.85; H, 2.42; N, 11.34. UV-vis ($\lambda_{max}$, nm (ε, M$^{-1}$ cm$^{-1}$), $CH_2Cl_2$ solution): 740(800), 575(2300), 320(13100). $^1$H NMR δ in (CDCl$_3$): dppz, 9.65(d, 1H, J=5.9Hz), 9.14(d, 1H, J=7.5Hz), 8.78(d, 1H, J=6.1Hz), 8.54(t, 1H, J=7.6Hz), 8.31(t, 1H, J=6.3Hz), 8.20(d, 1H, J=7.0Hz), 8.12(t, 1H, J=6.9Hz), 7.96(t, 1H, J=6.8Hz), 7.75(d, 1H, J=5.8Hz), 7.68(t, 1H, J=6.4Hz); NPh, 7.86(t, 2H, J=8.0Hz), 7.38(t, 1H, J=6.7 Hz), 7.14(d, 2H, J=8.1Hz).

### *[Re(OPPh$_3$)Cl$_3$(dppz)]ReO$_4$,* **(5)**

To 113 mg (0.14 mmol) of **3** in 20 mL acetonitrile dilute aqueous HNO$_3$ was added and the solution was stirred at room temperature for 0.25 h. During this time the solution colour changed from violet to yellow. Solvent removal under reduced pressure afforded [Re(OPPh$_3$)Cl$_3$(dppz)]ReO$_4$ as an yellow solid. The solid was washed thoroughly with water to remove the adherent nitric acid and then dried in vacuum over fused CaCl$_2$. Yield: 51 mg(69%). Anal. Calcd. for $C_{32}H_{22}Cl_3N_4O_5PRe_2$: C, 36.48; H, 2.39; N, 5.32. Found: C, 36.47; H, 2.35; N, 5.34. UV-vis ($\lambda_{max}$, nm (ε, M$^{-1}$ cm$^{-1}$), $CH_2Cl_2$ solution): 420(900), 320(11100). $^1$H NMR δ in (CDCl$_3$): dppz, 62.81(1H), 62.26(1H), 11.44(1H), 9.92(2H), 9.03(1H), 3.84 (2H), -70.08(1H), -95.04(1H); PPh$_3$, 10.42(6H), 7.91(6H), 7.49(3H). $\Lambda_M = 102\ \Omega^{-1}\ cm^2\ mol^{-1}$.

### *Synthesis of Re(PPh$_3$)Cl$_3$(dppz),***(6)**

To 73 mg (0.09 mmol) of complex **3** in 30 mL benzene 142 mg (0.54 mmol) of PPh$_3$ was added and the mixture was heated to reflux for 2 h. The resulting solution was evaporated to dryness and the residue was washed several times with hexane (to remove excess PPh$_3$). The residue was then dissolved in 5 mL dichloromethane and was subjected to chromatography on a silica gel column. A green band was eluted with benzene-acetonitrile (25:10) mixture. Solvent removal from the eluate under reduced pressure afforded Re(PPh$_3$)Cl$_3$(dppz) as a green solid. Yield: 61 mg (85%). Anal. Calcd. for $C_{32}H_{25}Cl_3N_4PRe$: C, 48.77; H, 3.20; N, 7.12. Found: C, 48.70; H, 3.25; N, 7.04. UV-vis ($\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$), $CH_2Cl_2$ solution): 660(1700), 590$^s$(1500), 465$^s$(3000), 310(23000). $^1$H NMR $\delta$ in (CDCl$_3$): dppz, 20.84(t, 1H, J=5.6Hz), 20.11(t, 1H, J=6.8Hz), 19.15(d, 1H, J=6.1Hz), 16.89(d, 1H, J=6.0Hz), 6.91(d, 1H, J=6.2 Hz), 6.63(d, 1H, J=7.1 Hz), 6.32 (d, 1H, J=6.3Hz), 5.98(t, 1H, J=7.9Hz), 1.08(t, 1H, J=7.1Hz), -1.98(d, 1H, J=6.4Hz); PPh$_3$ 14.18(d, 6H, J=6.6Hz), 9.27(t, 6H, J=7.5Hz), 8.91 (t, 3H, J=7.3Hz).

### *Rate Measurements*

A known excess of PPh$_3$ was added to a solution of [ReOCl$_3$(dppz)] (1.25x10$^{-4}$ M) in dichloromethane at the desired temperature and the thermostated reaction was followed spectrophotometrically (quartz cell, path length 1 cm) by measuring the absorbance ($A_t$) of the peak at 730 nm as a function of time, *t*. The absorbance $A_\alpha$ at the end of the reaction (24 h) was also measured. Values of $k_{obsd}$ and *k* were obtained from the slopes of the linear plots of $-\ln(A_\alpha - A_t)$ *versus t* and $k_{obs}$ *versus* [PPh$_3$] respectively. The activation enthalpy and entropy parameters were determined from the linear plot of $-[\ln kh/k_BT]$ *versus* $T^{-1}$ using the Eyring equation (Eq. 6).

$$k = (k_BT/\ h)[\exp(-\Delta H^\#/RT)\ \exp(\Delta S^\#/R] \qquad (6)$$

## Results and Discussion

### *Spectra*

In IR the oxido complex **2** displays the Re≡O stretch at 990 cm$^{-1}$, two Re–Cl stretches at 335 and 350 cm$^{-1}$ and two C=N stretches occur at 1608 and 1580 cm$^{-1}$. In the imido species **4** two Re–Cl stretches and two C=N stretches occur at 322**,** 341 and 1601, 1585 cm$^{-1}$ respectively. The rhenium(III) phosphine oxide complex **3** incorporating ReOP moiety displays a strong P=O stretch near 1127 cm$^{-1}$ while for the oxidised rhenium(IV) phosphine oxide complex **5** the P=O stretch appear at 1118 cm$^{-1}$ and a characteristic Re-O stretch of the $ReO_4^-$ anion at 903 cm$^{-1}$.

The oxido complex **2** display two absorption bands in the visible region near 760 and 470 nm respectively. The relatively low intensity band near 760 nm is consistent with substantial contribution from the ligand field transition $d_{xy} \rightarrow d_{xz}$, $d_{yz}$. The imido complex **4** also display a similar band at slightly higher energy (740 nm). The phosphine oxide complex **3** display two main bands in the visible region near730 and 580 nm associated with a number of shoulders. These are believed to be of MLCT origin. The spectra are of diagnostic value and have been employed in rate studies (vide infra). Trivalent rhenium is a potent $\pi$-donor and the metal oxidation is expected to diminish the donor power significantly[2,5,13]. Thus upon metal oxidation from rhenium(III) phosphine oxide **3** to rhenium(IV) phosphine oxide**5** the MLCT band disappears and the lowest energy band now occurs near 420 nm. the phosphine complex **6** shows several bands in the visible region with a prominent feature near 660 nm. This is assigned to MLCT excitation and is believed to correspond to the band near 730 nm in the phosphine oxide species noted above. The blue shift in going from phosphine oxide to phosphine complex is consistent with the extra stabilization of the $t_{2g}$ shell by the phosphine donor. The oxido and imido complexes are both diamagnetic ($d_{xy}^2$) and give rise to well resolved $^1$H NMR lines. Chemical shifts and coupling constants for the complexes are listed in the experimental section. The phosphine oxide complex **3** and the phosphine chelate **6** have magnetic moment value of 2.08 µB and 2.14 µB as in several other rhenium(III) species and the $^1$H NMR spectra is found to be paramagnetically shifted[2,5,13,14]. The spectra of Re(NPh)Cl$_3$(dppz), Re(OPPh$_3$)Cl$_3$(dppz), [Re(OPPh$_3$)Cl$_3$(dppz)]ReO$_4$ and Re(PPh$_3$)Cl$_3$(dppz) are shown in Figure 1.

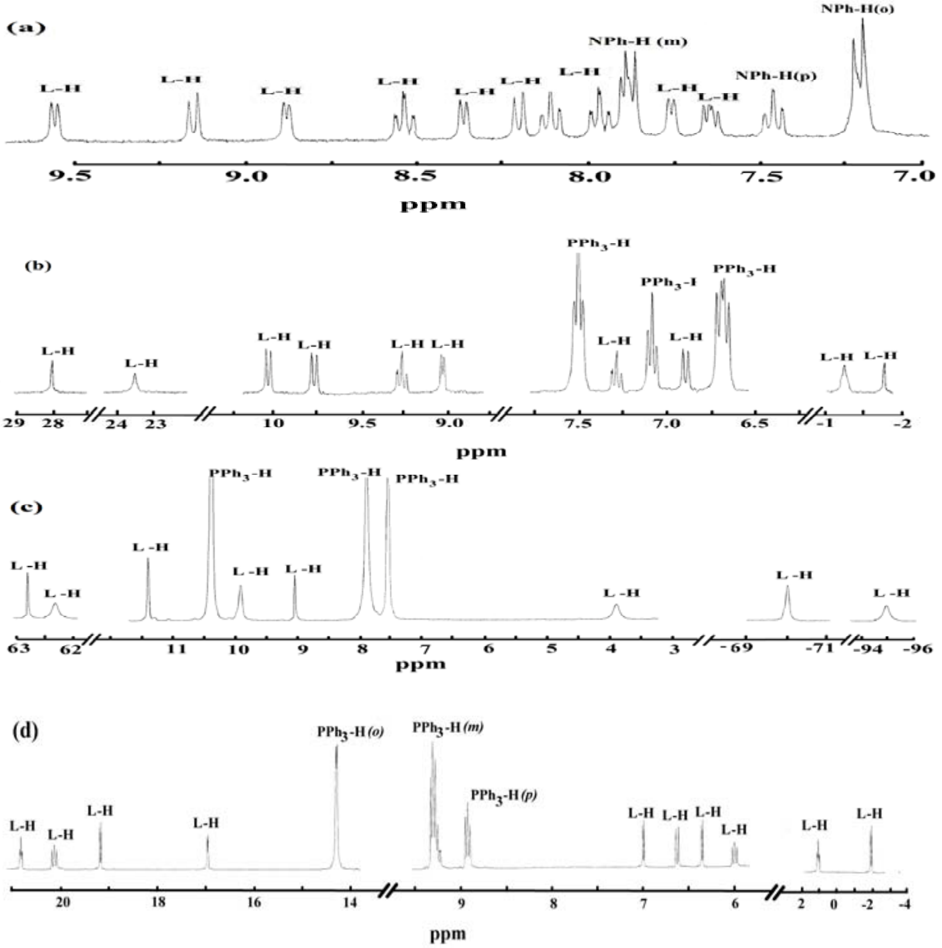


**Figure 1**. $^1$H NMR spectra in $CDCl_3$ solution of (a) $Re(NPh)Cl_3(dppz)$ (b) $Re(OPPh_3)Cl_3(dppz)$ (c) $[Re(OPPh_3)Cl_3(dppz)]ReO_4$ (d) $Re(PPh_3)Cl_3(dppz)$, the L-H protons corresponds to dppz protons, NPh-H corresponds to amine protons and $PPh_3$-H corresponds to phosphine protons.

### *Metal redox*

The complexes are uniformly electroactive in acetonitrile solution. The oxido and the imido species display quasireversible (peak-to-peak separation 80-100 mV) one-electron response corresponding to $Re^{VI}/Re^{V}$ couple having $E_{1/2}$ of 1.58 and 0.88 V *versus* SCE respectively signifying superior stabilization of $Re^{VI}$ state upon imido coordination as compared to oxido coordination. Clearly defined metal reduction (say from +5 to +4 or +3 states) could not be observed electrochemically. However, chemical reduction of the oxido complex is readily achieved. Thus tertiary phosphine affords trivalent phosphine oxide complex **3** (Eq. 2) which display one-electron response near 0.30 V (peak to peak separation 80 mV) corresponding to $Re^{IV}/Re^{III}$ couple. The rhenium(IV) species **5** have the same voltammogram (opposite scan direction) as **3**. In the phosphine complex **6** the $Re^{IV}/Re^{III}$ reduction potential lie near 0.60 V with peak-to-peak separation of 85 mV. The increase in the reduction potential in the phosphine complex is consistent with the stabilization of $t_{2g}$ shell *via* back-bonding to phosphorus. The voltammograms of $ReOCl_3(dppz)$, $Re(NPh)Cl_3(dppz)$, $Re(OPPh_3)Cl_3(dppz)$ and $Re(PPh_3)Cl_3(dppz)$ are shown in Figure 2.

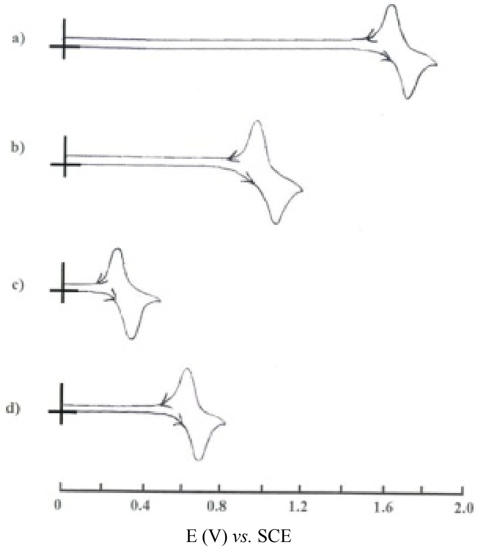
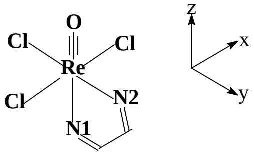


**Figure 2**. Cyclic voltammogram of a) $ReOCl_3(dppz)$ b) $Re(NPh)Cl_3(dppz)$ c) $Re(OPPh_3)Cl_3$ (dppz) d) $Re(PPh_3)Cl_3(dppz)$ in acetonitrile solution.

### *Bonding and isomer preference*

Some qualitative aspects of bonding in $ReOCl_3(dppz)$ will be considered assuming the idealized geometry, **7** with $Re{\equiv}O$ defining the z-axis. The filled $p_z$ orbital of the oxido oxygen atom is used for the $\sigma$-hybridization and the filled $p_x$, $p_y$ orbitals are used for $\pi$-bonding with metal $d_{xz}$, $d_{yz}$ orbitals. The latter orbitals are destabilized and the two metal electrons ($Re^V$, $5d^2$) occupy the $d_{xy}$ orbital in a paired configuration. A relatively weak band observed near 760 nm (*vide infra*) is tentatively assigned to $d_{xy}{\rightarrow}d_{xz}$, $d_{yz}$ transition.



**7**

The filled $d_{xy}$ orbital can interact with the empty pyridazine $\pi^*(C{=}N)$ orbital, the sense of electron donation being $Re{\rightarrow}\pi^*$. A synergestic $\pi$ interaction of type $\pi^*{\leftarrow}Re{\leftarrow}O$ is thus possible, provided the pyridazine nitrogen and the oxido oxygen atoms lie *cis* to each other as in the observed structure.

Steric and electronic factors alone are expected to favour meridional geometry as observed in the cases of $ReOCl_3(dppz)$ and $Re(NPh)Cl_3(dppz)$. Like the oxido and imido ligands the $OPPh_3$ ligands are pure donors and optimum metal-ligand bonding is achievable in the meridional geometry, there being no bonding advantage for the sterically unfavourable facial disposition of ligands. It is thus logical that $Re(OPPh_3)Cl_3(dppz)$ assumes meridional geometry like the oxido and the imido species. Upon substitution of $OPPh_3$ by $PPh_3$ the bonding situation changes considerably due to phosphine $\pi$-acidity, the concerned orbitals being a mixture of 3d$\pi$ and P-C $\sigma^*$ components[16]. There are thus two good $\pi$-acceptors in the phosphine complexes: dppz and $PPh_3$. The back-bonding effect is maximized in the facial disposition which ensures minimum competition between the two ligands for identical metal orbitals. The observed geometrical selectivity is strong and exclusive. In no case isomers have been observed for the same complex. The strong geometrical discrimination by phosphine oxide and phosphine ligands is emerging as a general phenomenon[2,5,13,14,15] for $ReCl_3(NN)$ complexes where NN is a chelated $\pi$-acidic ligand. The present dipyridylpyridazine complexes augment this class.

### *Oxygen atom transfer*

The variable-temperature rates of the reaction of Eq. 2 have been studied spectrophotometrically in $CH_2Cl_2$ solution. Time evolution spectra are characterized by isosbestic point is shown in Figure 3. Under pseudo-first order condition (excess $PPh_3$), the rates are proportional to the concentration of the oxido complex and the observed rate constant, $k_{obsd}$, is proportional to the concentration of $PPh_3$. The reaction law is thus second order (Eq. 7).

$$\begin{aligned}\text{Rate} &= k_{obsd}\,[ReOCl_3(dppz)] \\ &= k\,[ReOCl_3(dppz)]\,[PPh_3] \qquad (7)\end{aligned}$$

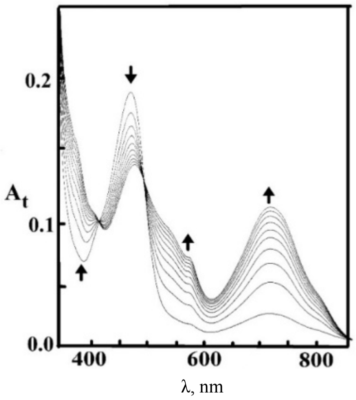
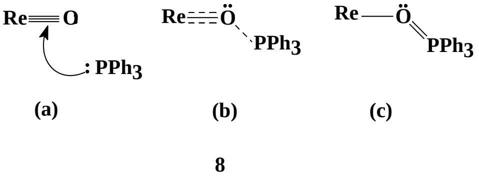


**Figure 3.** Time evolution spectra for the reaction of $ReOCl_3(dppz)$ with $PPh_3$ in $CH_2Cl_2$ solution at 302 K

The rate constant $k$ follows the Eyring equation (Eq. 6). Rate data and the activation parameters are listed in Table 1. The negative entropy of activation of the oxygen atom transfer process as revealed in the reaction of $[ReOCl_3(dppz)]$ with $PPh_3$ is consistent with an associative transition state. A probable model for the association and progress of the reaction is stylized in **8** which is constructed in the light of previous work and the findings of oxygen atom transfer reactions involving $Mo^{VI}O_2$ and $W^{VI}O_2$ species[3-5].



**8**

In **8** the full and broken lines, respectively, represent coordinate covalent bonds and weak links. Following attack on π*(ReO) orbitals by the phosphine lone pair (**8a**), the *π*-bonds are weakened and a O---P link is established (**8b**, transition state). In the end, the P=O bond remains coordinated to the metal as in **8c**.

**Table 1.** Rate constants for the reaction of [$ReOCl_3$(dppz)] + $PPh_3$→ [$Re(OPPh_3)Cl_3$(dppz)] in dichloromethane solution[a,b].

| T, *K* | $10^2$, $PPh_3$ | $10^5k_{obsd}$, $s^{-1}$ | $10^3k$, $M^{-1}s^{-1}$ | |
|---|---|---|---|---|
| 302 | 1.06 | 7.028 | 6.63 (0.03) | $\Delta H^{\#}$ = 16.06(0.1) kcal $mol^{-1}$ |
| | 1.40 | 9.250 | | |
| | 2.00 | 13.258 | | |
| 305 | 1.06 | 9.080 | 8.72 (0.02) | $\Delta S^{\#}$ = -15.80(0.3) cal $K^{-1}$ $mol^{-1}$ |
| | 1.40 | 12.027 | | |
| | 2.00 | 17.273 | | |
| 308 | 1.06 | 11.601 | 11.35 (0.05) | |
| | 1.40 | 15.506 | | |
| | 2.00 | 22.280 | | |

[a] *The initial concentration of [$ReOCl_3$(dppz)] is 1.25x$10^{-4}$ M.* [b] *Least-squares deviations are given in parentheses*

## Conclusion

Oxidorhenium(V) complex of dipyridylpyridazine has been isolated in the form of $ReOCl_3$(dppz) from which the corresponding $Re^{III}(OPPh_3)Cl_3$(dppz) and $Re^{V}(NPh)Cl_3$ (dppz) species have been prepared. The reactions are stereoretentive, the $ReCl_3$ moiety being uniformly meridional in geometry. The phosphine oxide complex of the trivalent rhenium is chemically oxidized to rhenium(IV) congener. Displacement of coordinated phosphine oxide by phosphine is attended with *meridional→facial* geometrical transformation.

The oxidorhenium(V) and the imidorhenium(V) complexes are uniformly diamagnetic and a relatively weak band in the region 740-760 nm is believed to have considerable ligand field character. The quasireversible one-electron $Re^{VI}/Re^{V}$ reduction potential is much higher in the oxido complex (1.58 V) than in the imido (0.88 V) complex signifying superior stabilization of the hexavalent state upon imido coordination. Rhenium(III) phosphine oxide complex show two bands in the visible region near 730 and 470 nm while for the phosphine complex prominent feature is observed around 660 nm. The quasireversible one-electron $Re^{IV}/Re^{III}$ reduction potential is much higher in the phosphine complex (0.60 V) than in the phosphine oxide (0.30 V) complex. The blue shift of the MLCT excitation in going from the phosphine oxide to phosphine complex and the increase in the reduction potential in the phosphine complex is consistent with the extra stabilization of the $t_{2g}$ shell via back-bonding to phosphorus. Upon metal oxidation from rhenium(III) phosphine oxide to rhenium(IV) phosphine oxide the MLCT band disappears and the lowest energy band in the rhenium(IV) complex occurs near 420 nm signifying considerable reduction of *π*-donor power of trivalent rhenium upon metal oxidation. The rates and activation parameters of the bimolecular oxygen atom transfer process have been quantitated. The entropy of activation is negative consistent with an associative model.

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